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Dated 17 March 2003

INVESTOR IN PEOPLE

GB0205592.9

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

CDT OXFORD LIMITED,
Incorporated n the United Kingdom,
Greenwich House,
Madingley Rise, Madingley Road,
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United Kingdom

[ADP No. 08541435001]

The Patent Office

INVESTOR IN PEOPLE

GB0205592.9

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

SECTION 30 (1977 ACT) APPLICATION FILED : 9/1/03

OPSYS UK LIMITED,
Incorporated in the United Kingdom,
2 Temple Back,
East Temple Quay,
BRISTOL,
United Kingdom

[ADP No. 08534729001]

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11MAR02 E702276-1 D00085
P01/7700 0.00-0205592.9

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1. Your reference — SJW/8349

0205592.9
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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Opsys Limited
Unit 8 Begbroke Business Park
Sandy Lane
Yarnton
Oxfordshire OX5 1PF
United Kingdom

SECTION 30 (1977 ACT) APPLICATION FILED 12/12/02

Patents ADP number *(if you know it)* — 7941396001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

"Polymerisable Compositions and Organic Light-Emitting Devices Containing Them"

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Stevens Hewlett & Perkins
1 St. Augustine's Place
Bristol BS1 4UD
United Kingdom

Patents ADP number *(if you know it)* — 1545002

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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Signature Stevens Hewlett + Perkins Date 08/03/02

STEVENS HEWLETT & PERKINS

12. Name and daytime telephone number of person to contact in the United Kingdom

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POLYMERISABLE COMPOSITIONS AND ORGANIC LIGHT-EMITTING DEVICES CONTAINING THEM

Background to the Invention

Organic light emitting diodes (OLEDs) are an emerging display technology. In essence an OLED (or organic electroluminescent device) comprises a thin organic layer or stack of organic layers sandwiched between two electrodes, such that when a voltage is applied, visible light is emitted. At least one of the electrodes must be transparent to visible light.

There are two principle techniques that can be used to deposit the organic layers in an OLED: thermal evaporation and solution processing. Solution processing has the potential to be the lower cost technique due to its potentially greater throughput and ability to handle large substrate sizes. However, several manufacturing issues still have to be resolved before solution processing of OLEDs can fulfil its potential. In a multi-colour or full-colour display the emissive organic layers need to be patterned according to the pixel layout. High-resolution displays require a high-resolution pattern for the emissive layer. To date, solution-processing techniques for patterning the emissive layer are far from ideal.

In many cases, the most efficient OLED devices have multi-layer structures (fluorescent emitter: e.g. US 5,719,467 (Hewlett-Packard 1995). EP 0,921,578 (CDT 1998). US 6,048,573 (Kodak 1998). US 6,069,442 (Kodak 1997). US 5,554,450 (Kodak 1995) phosphorescent emitter: e.g. WO 00/57676 and US 6303238). Such multi-layer structures can be formed by thermal evaporation, but when solution-processing techniques are used, depositing a second layer may wash away the first layer.

It has been recognised that if a photolithographic technique could be successfully applied to the patterning of the organic layers in an OLED then this would offer many benefits. Photolithographic techniques are established in other industries and can give good resolution and high throughput. However the attempts to use photolithography during the formation of the organic layers in OLEDs have all had only very limited success.

BASF (US 5518824) discusses the principle of forming an OLED using a crosslinkable charge-transporting material. The proposed functional groups are acrylates, vinylethers and epoxides. The material is deposited from solution, and then exposed to UV light, which crosslinks the material making it insoluble. Subsequent luminescent or electron transporting layers can be deposited on top of the insoluble layer. BASF mentions that if the UV exposure is carried out through a mask, then the exposed areas will be insoluble and the unexposed areas still soluble, and developing (washing) this film in solvent will remove the unexposed material, leaving the insoluble patterned material. However, this patterning is not demonstrated. BASF discuss doping the film with a fluorescent dye or using a crosslinkable fluorescent dye (US 5922481) to form the light-emitting layer. The EL device results reported by BASF from its crosslinked devices are very poor. The two devices reported, which have crosslinked but un-patterned light emitting layers, give light emission only at 87 V and 91 V, respectively, both of which are entirely unacceptable operating voltages for an OLED. Canon (EP 1146574 A2) also demonstrate an OLED with a crosslinked emissive film, but there is still no demonstration of a patterned emissive layer. Further, Bacher et al. (Macromolecules 1999, 32, 4551-4557) demonstrated photo-crosslinking of a hole-transporting (acrylate derivative of triphenylene) material. They produced a patterned photo-crosslinked hole-transport layer on to which they deposited an emissive layer (tris(8-hydroxyquinoline)aluminium: Alq_3), and made a functioning OLED device. However, they had not developed a technique for photo-lithographically patterning the emissive layer, and unless the emissive layer can also be patterned, only a monochrome device can be formed. The problem with acrylates in all the prior art is that although the acrylates can give very high resolution in the patterning process, they quench luminescence. The quenching of fluorescence by carbonyl groups is well known (Becker, Theory and Interpretation of Fluorescence and Phosphorescence, Wiley Interscience, NY 1969).

Other authors suggest crosslinking materials by thermally-initiated processes. While such processes do form insoluble films allowing subsequent layers to be deposited on top, they do not allow patterning of the layer. IBM has a patent (US 6107452) on thermally/photochemically-induced crosslinking of polymers for use, for example, in light-emitting devices. No patterning was demonstrated.

Bayerl et al. (Macromolecules 1999, 20, 224-228) used crosslinked oxetane-bisfunctionalized N,N,N',N'-tetraphenyl-benzidine as the hole-transporting material in a two-layer device. However, they did not pattern the hole-transporting material. Further work on oxetanes by Meerholz et al. (WO 02/10129) uses cationic photopolymerization to form crosslinked layers. In one instance the emissive layer was patterned. But in many cases the photoacid generated during the polymerization would attack other components of an OLED, in particular organometallic materials, and therefore such procedures would not generally be appropriate for the formation of patterned crosslinked emissive layers in OLED devices.

Photo-polymerisable thiol/ene systems are known for various applications such as printing plates and protective coatings. In these prior applications of thiol/ene systems the resulting polymers have been insulators. Most of the thiol/ene systems mentioned in the prior art contain non-conjugated carbonyl groups rather than aliphatic thiols, as aliphatic thiols can retain a nasty smell. In particular PETMP (Pentaerythritol tetrakis(3-mercaptopropionate) is commonly used as the thiol component (e.g. US 5100929 and US 5167882).

The present invention is directed to OLEDs that solve some of the problems in the prior art.

Summary of the current invention

The current invention is about a composition of a mixture of a thiol material and an ene material that can be polymerised to form a charge-transporting or luminescent film.

The current invention is about an OLED comprising a charge-transporting or emissive layer that has been formed by polymerising a thiol material and an ene material.

The current invention is also about a process for forming such an OLED that includes depositing a layer of material comprising a thiol and an ene, from solution, exposing said layer to actinic radiation (UV light, visible light, electron beams or X-rays), through a mask, and then optionally developing said film.

According to a first aspect of the current invention there is provided a composition comprising a mixture of at least one monomer with the formula:

$$A\text{–}(X)_n \qquad (1)$$

and at least one monomer with the formula:

$$B\text{–}(Y)_m \qquad (2)$$

where monomers of formula (1) are polymerisable with monomers of formula (2), n and m are integers greater than or equal to 2, such that n and m may be the same or different, X is a group containing a terminal thiol, Y is a group containing a reactive unsaturated carbon-carbon bond, each X may be the same or different, each Y may be the same or different, and A and B are molecular fragments such that at least one of A or B is an organic charge-transporting or organic light-emitting fragment.

According to a second aspect there is a solid film comprising a thermally-induced or radiation-induced polymerisation reaction product of a composition according to the first aspect of the invention.

According to a third aspect of the present invention there is provided a solid film comprising a polymer with repeat unit

$$\text{-(A-Z-B-W)-} \qquad (3)$$

where A and B are as defined above, Z is the addition product of the thiol-containing group, X, and the group containing a reactive unsaturated carbon-carbon bond, Y, and W is the addition product of the group containing a reactive unsaturated carbon-carbon bond, Y and the thiol-containing group, X.

According to a fourth aspect of the invention there is provided an OLED device comprising, laminated in sequence, a substrate, a first electrode, a first optional charge-transporting layer, a light-emitting layer, a second optional charge-transporting layer and a counter electrode wherein at least one of the optional charge-transporting layers and/or the light-emitting layer is according to the second or third aspects of the invention.

In a further aspect of the invention there is provided a process for forming a charge-transporting or emissive layer in an OLED comprising the following steps:

i) depositing a film with a composition according to the first aspect of the invention
ii) exposing said film to actinic radiation, or more preferably visible or UV light.

In yet a further aspect of the invention there is provided a process for forming a charge-transporting or emissive layer in an OLED comprising the following steps:
i) depositing a film with a composition according to the first aspect of the invention
ii) exposing said film to actinic radiation, or more preferably visible or UV light through a mask
iii) washing the exposed film to remove any unexposed material.

Detailed description of the current invention

According to the present invention there is provided a composition comprising a mixture of at least one monomer with the formula:

$$A\text{–}(X)_n \qquad (1)$$

and at least one monomer with the formula:

$$B\text{–}(Y)_m \qquad (2)$$

where monomers of formula (1) are polymerisable with monomers of formula (2), n and m are integers greater than or equal to 2, such that n and m may be the same or different, X is a group containing a terminal thiol, Y is a group containing a reactive unsaturated carbon-carbon bond, each X may be the same or different, each Y may be the same or different, and A and B are molecular fragments such that at least one of A or B is an organic charge-transporting or organic light-emitting fragment.

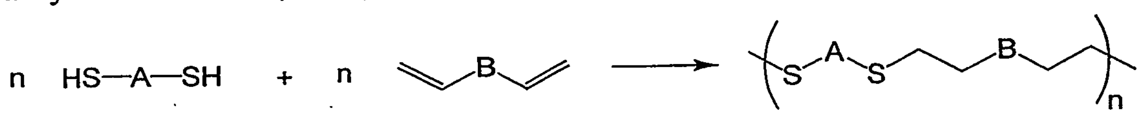
The term reactive unsaturated carbon-carbon bond means a group that will react under the correct conditions with a thiol to form a thioether linkage. Reactive unsaturated carbon-carbon groups are those with carbon-carbon double or triple bonds such as alkenes, alkynes and strained ring systems. In contrast the unsaturated carbon-carbon bonds in an aromatic ring would not react with a thiol to give a thioether linkage and so are un-reactive groups. Reactive unsaturated carbon-carbon bonds are often located at a terminal position in the chain or branch.

X and Y are groups capable of undergoing free-radical induced polymerisation. Optionally, the free-radical induced polymerisation can take place in the presence of a radical initiator. It is desirable that the resulting polymer is insoluble in a solvent that

can be used to wash off the un-reacted monomers. Therefore, it is preferred that a crosslinked polymer network is formed, i.e. that $n + m > 4$. The exposure to actinic radiation is preferably done in an inert atmosphere to avoid the formation of peroxy groups in the polymer. Following washing or developing of the film, the film may be dried or undergo other post-patterning treatment.

There may be other components in the film in addition to the thiol monomer and the monomer containing a reactive unsaturated carbon-carbon bond. In particular there may be a radical initiator, a luminescent dopant, or a charge-transporting molecule in the mixture.

X and Y are groups capable of undergoing photo-initiated free-radical induced polymerisation. X is a group containing a terminal thiol. Y is a group containing a reactive unsaturated carbon-carbon bond or part of an unsaturated strained ring system. For brevity such a group is sometimes referred to as an ene. X and Y are preferably connected to A and B by spacer units. Under the correct conditions X and Y react to form a thioether linkage. The reaction proceeds by a step growth mechanism, as illustrated in the reaction scheme below (Jacobine, Radiat. Curing Polym. Sci. Technol., 1993, 3, 219-68).



Here, for illustration, the ene is a double bond but it could be a triple bond or an unsaturated strained ring system. Initiation involves the formation of thiyl radicals. Then a thiyl radical attacks the reactive double bond, Y, to give a β-thioether carbon radical, which then abstracts a hydrogen from another thiol group, creating a new thiyl radical, which can propagate the reaction. The thiol is effectively added across the reactive double bond and the chain transferred, hence the need for multi-functional monomers. If each monomer has two functional groups ($n=m=2$) then a linear polymer can be formed, if at least one of n or m is greater than 2 then a crosslinked polymer can be formed.

In principle, as many X groups as Y groups should be present for complete reaction to occur, if one group is in excess then the excess will remain un-reacted. However, as is well known, in a polymerisation reaction of multi-functional monomers assuming unlimited mobility not all functional groups react (P. J. Flory, J. Am. Chem. Soc. 1947, 69, 2893), so it is not thought to be critical that the number of X and Y groups is balanced.

The polymerisation reaction produce of the thiol monomer (1) and the ene monomer (2) is a polymer with repeat unit

-(A-Z-B-W)- (3)

where A and B are as defined above, Z is the addition product of the thiol-containing group, X, and the reactive unsaturated carbon-carbon bond, Y, and W is the addition product of the reactive unsaturated carbon-carbon bond, Y and the thiol-containing group, X. Such a polymer comprises a further aspect of the invention.

If A and B have similar molecular weights, both A and B should contain charge-transporting or emissive groups, i.e. be functional. If A and B have dissimilar molecular weights, however, it would be possible for the high molecular weight (i.e. oligomeric) group to be charge transporting or emissive while the low molecular weight group is neither charge transporting nor emissive. However, the resulting polymerised film should have electroluminescent or charge-transporting properties.

The fragments A and B can have different properties depending on required function of the photopolymer layer. In one embodiment, the photopolymer functions as a charge-transport layer in an OLED. In this case preferably both fragments, A and B, should contain charge-transporting groups, unless one fragment has much higher molecular weight than the other in which case said fragment alone can be charge-transporting. In another embodiment the photo-polymer forms the emissive layer. In this case, one or both organic fragments can be a light-emitting fragment and the fragments that are not light-emitting are preferably charge transporting, so for example one of A or B is a light-emitting fragment and the other is a charge-transporting fragment. Alternatively neither fragment A nor B is light-emitting but the photopolymer is used as a charge-transporting host matrix for an emissive dopant. If one fragment has much higher molecular weight than the other, said fragment alone

can be charge transporting or emissive. It is also possible for an emissive dopant to be used with a photopolymer host that is itself emissive, i.e. where at least one of A and B is a light-emitting fragment.

The invention also provides an OLED device comprising, laminated in sequence, a substrate, a first electrode, a first optional charge-transporting layer, a light-emitting layer, a second optional charge-transporting layer and a counter electrode wherein at least one of the optional charge-transporting layers and/or the light-emitting layer is a solid film comprising a polymerisation reaction product of a composition comprising a mixture of at least two components with the following formulae:

$A\text{–}(X)_n$ $B\text{–}(Y)_m$,

where monomers of one component are polymerisable with monomers of the other component, n and m are integers greater than or equal to 2, such that n and m may be the same or different, X represents a group containing a terminal thiol and Y represents a group containing a reactive unsaturated carbon-carbon bond, and A and B are molecular fragments such that at least one of A or B is an organic charge-transporting or organic (visible) light-emitting fragment.

The invention also provides a method for making such an OLED, whereby the charge-transporting and/or light-emitting film is made by the process of:

i) depositing a film with a composition according to this invention

ii) exposing said film to actinic radiation, or more preferably visible or UV light, optionally through a mask,

iii) optionally washing the exposed film to remove any unexposed material to leave a pre-determined pattern.

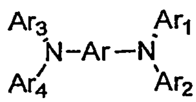
In a typical type of OLED the first electrode is an anode, the first optional charge-transporting layer is a hole-transporting layer, the second charge-transporting layer is an electron-transporting layer, and the counter electrode is a cathode. However in another embodiment the first electrode is a cathode, the first optional charge-transporting layer is an electron-transporting layer, the second charge-transporting layer is a hole-transporting layer, and the counter electrode is an anode. As is well known in the field there may be additional functional layers in the OLED. If the light emitter is phosphorescent, it is particularly beneficially that either the electron-

transporting layer also functions as a hole-blocking layer, or there is an additional hole-blocking layer between the light-emitting layer and the electron-transporting layer. A pixellated OLED display can either be a passive-matrix or an active-matrix display. In one embodiment the first charge-transporting layer is a polymerised film according to this invention. In a preferred embodiment the light-emitting layer is a polymerised film according to this invention. In an alternative embodiment, both the first charge-transporting layer and the light-emitting layer are polymerised films according to this invention. It would also be possible for the first charge-transporting layer, the light-emitting layer and the second charge-transporting layer to all be polymerised films according to this invention.

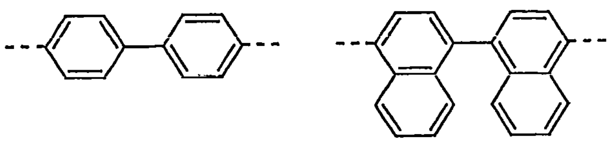
The light-emitting layer in the OLED is preferably patterned, that is a suitable photo-mask is used when the film is exposed to light. This patterning technique allows a multi-colour OLED to be formed. A key advantage of the thiol-ene system is that good resolution can be achieved when it is photo-patterned. A film that is capable of emitting a first colour is deposited, patterned and developed to form pixels capable of emitting a first colour. At this stage, since the film of the first colour is insoluble, it allows a film of a material that is capable of emitting a second colour to be deposited without disrupting the first colour film. This second film is patterned and developed to form pixels capable of emitting the second colour. The process can be repeated to deposit a material capable of emitting a third colour. If present, it may be appropriate to pattern a charge-transporting layer, and this can be done using the same masking technique.

A solution-processing technique, such as spin-coating, ink-jet printing, dip-coating meniscus or roller coating, or other printing or coating technique, or thermal-transfer method is used to deposit the thiol/ene layer which is to be polymerised.

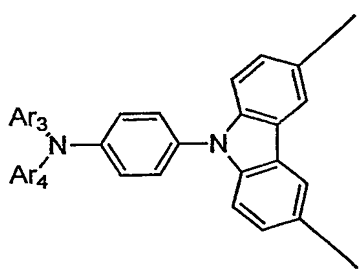
As discussed above, the fragments A and B can contain charge-transporting units. Suitable hole-transporting materials contain π-electron rich moieties. Particularly suitable are triarylamines (for examples see Shirota, J. Mater. Chem., 2000, 10, 1 – 25). The charge-transporting fragment A or B can be based on known hole-transporting arylamine materials such as those with the formula



where Ar is an optionally substituted aromatic group, such as phenyl, or



and Ar_1, Ar_2, Ar_3 and Ar_4 are optionally substituted aromatic or heteroaromatic groups (Shi et al (Kodak) US 5,554,450. Van Slyke et al, US 5,061,569. So et al (Motorola) US 5,853,905 (1997)). In the current invention at least two of Ar_1, Ar_2, Ar_3 and Ar_4 are bonded to either a thiol group, X, or a group containing a reactive unsaturated carbon-carbon bond, Y. Ar_1 and Ar_2, and/or Ar_3 and Ar_4 are optionally linked to form a N containing ring, for example so that the N forms part of a carbazole unit e.g.



Bipolar materials that can form a bipolar fragment A or B transport both holes and electrons. Suitable materials preferably contain at least two carbazole units (Shirota, J. Mater. Chem., 2000, 10, 1-25).

Electron-transporting materials that can form an electron-transporting fragment A or B contain π-electron deficient moieties. Examples of suitable π-electron deficient moieties are oxadiazoles, triazines, pyridine, pyrimidine, quinoline, and quinoxaline (Thelakkat, Schmidt, Polym. Adv. Technol. 1998, 9, 429-42). Specific examples include Alq_3 [Aluminium tri(8-hydroxyquinoline)], TAZ (3-phenyl-4-(1-naphthyl)-5-phenyl-1,2,4-triazole) and OXD-7 (1,3-bis(N,N-t-butyl-phenyl)-1,3,4-oxadiazole).

Light emission may be via fluorescence or phosphorescence.

According to IUPAC fluorescence is defined as spontaneous emission of radiation (luminescence) from an excited molecular entity with the formation of a molecular entity of the same spin multiplicity. Suitable fluorescent light-emitting materials are many organic molecules and complexes of metals of group 2, 12, 13 or light d-block metals with organic ligands. According to the colour of the light emission these materials can be divided into three groups, blue, green and red emitters.

Suitable fluorescent blue emitters are e.g. stilbenes, coumarins, anthracences (Kodak US 5,972,247 (1999).Toshio et al (Toyo Ink) EP 0765106 (1996)) and perylenes (So et al (Motorola) US 5,853,905 (1997). Lee et al (Motorola) US 5,747,183 (1996)). Also suitable are blue-emitting aluminium complexes (Bryan et al (Kodak) US 5,141,671. Van Slyke et al (Kodak) US 5,150,006)). Suitable green emitters are Alq_3 (Chen and Tang, Macromol. Symp. 1997, 125, 1-48), coumarins (Chen et al (Kodak) US 6,020,078) and quinacridone (Shi et al (Kodak) US 5,593,788). Suitable red emitters are DCM and its derivatives (Chen et al, US 5,908,581). The fluorescent material can be a molecular or dendritic species. For examples of suitable fluorescent dendrimers see Samuel et al. (WO 99/21935). The light-emitting material may be a dopant in the crosslinked charge-transporting matrix (comprising charge-transporting fragments A and/or B), in which case the emission spectrum of the charge-transporting matrix should overlap the absorption spectrum of the light-emitting dopant. Alternatively, the light-emitting material may be modified so that it is itself a monomer, i.e. the light emitting material is the fragment A or B of a polymerisable material. The dopant can be a single material or a mixture of compounds. The concentration of the dopants is chosen so as to maximise colour purity, efficiency, and lifetime.

According to IUPAC the term phosphorescence designates luminescence involving change in spin multiplicity, typically from triplet to singlet or vice versa. The luminescence from a quartet state to a doublet state is also phosphorescence.
Suitable phosphorescent light-emitting materials are heavy transition metal complexes. In particular organometallic complexes of iridium for example $Ir(ppy)_3$ (*fac* tris(2-phenylpyridine)iridium), which gives green emission (see Baldo et al., *Appl. Phys. Lett.*, **75** no.1, 1999, 4), or $(btp_2)Ir(acac)$ (bis(2-(2'-benzo[4,5-α]thienyl)

pyridinato-N,C$^{3'}$) iridium (acetyl-acetonate)), which gives red emission (see Adachi et al., *Appl. Phys. Lett.*, 78 no.11, 2001, 1622) are suitable. It could also be a complex of platinum, for example 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP) which gives red emission. The phosphorescent material can be a molecular or dendritic species. The light-emitting material may be a dopant in the crosslinked charge-transporting matrix (comprising charge-transporting fragments A and/or B), in which case the charge-transporting can be bipolar, hole transporting or electron-transporting. Alternatively, the light-emitting material may be modified so that it is itself a monomer, i.e. the light-emitting material is the fragment A or B of a crosslinkable material. The dopant can be a single material or a mixture of compounds. The concentration of the dopants is chosen so as to maximise colour purity, efficiency, and lifetime.

The concentration of the phosphorescent light-emitting fragment in the host material should be such that the film has a high photoluminescent and electroluminescent efficiency. If the concentration of the emissive species is too high, quenching of luminescence can occur. A concentration in the range 0.01-49 molar %, is generally appropriate.

Preferred examples of thiol monomers and ene monomers, suitable for use with a phosphorescent dopant, are shown in figures 1 and 2, respectively. A di-functional monomer derivative of CBP used with a tri-functional monomer derivative of TCTA will form a crosslinked polymer. Alternatively a crosslinked polymer would be formed if both the thiol and ene monomers were tri-functional derivatives of TCTA.

There is typically a spacer chain between the charge-transporting or light-emitting moiety and the polymerisable thiol or the reactive unsaturated carbon-carbon bond. Such a spacer improves the film forming properties of the material, allowing good quality films to be deposited from solution. The spacer also aids the polymerisation process. The spacer should not contain any carbonyl groups (including those in the form of esters, amides etc.). The spacer can comprise alkyl, ether, thioether, aryl, siloxane, amine or unsaturated groups, or heteroatoms such as silicon, boron or phosphorus. In fact neither A–$(X)_n$ nor B-$(Y)_m$ should contain any carbonyl groups.

Synthetic routes to form thiol-containing materials including those starting from thiourea, thiosulfate ions, thiol esters and dithiocarbamates can be found in S. Patai, *Chapter 4, The Chemistry of the Thiol Groups,* John Wiley & Sons, London 1974.

A synthetic route to alkene materials that have an ether linkage between the reactive unsaturated carbon-carbon bond and the rest of the molecule, is via a nucleophilic substitution in the presence of base as shown in figure 2 (the step from compound 10c to compound 10). *Synthesis of ethers, Houben-Weyl, Methoden der organische Chemie, V1/3,* Georg Thieme Verlag, Stuttgart 1965.

Thiol-ene mixtures can be easily thermally-polymerized and photo-polymerised. Photo-polymerization has the advantage that good resolution patterned films can be obtained and hence photo-polymerization is preferred for OLED applications. The reactive unsaturated carbon-carbon bonds are preferably electron-rich or they form part of a strained ring system. In this later case, reaction of the unsaturated carbon-carbon bond with a thiol will then release the ring strain. The reactive unsaturated group consists preferably of a norbornyl or vinylether moiety, other useful enes consist of allylether, or unsaturated cyclic systems. For the thiol-ene systems there are suitable initiators for activation by either UV light or visible light. For successful initiation, it is generally preferable to use a wavelength of light that is absorbed by the initiator but not strongly absorbed by the other components of the film. In this way the initiator functions well and photo-degradation of the film is minimised.

The thiol-ene systems mentioned here do not contain any carbonyl groups therefore no quenching of luminescence is observed. Unlike previously proposed photo-polymerisable systems proposed for OLEDs the thiol-ene systems is unique in offering a combination of high-resolution patterning with minimum luminescence quenching.

CLAIMS

1. A composition comprising a mixture of at least one monomer with the formula:

$$A{-}(X)_n \qquad (1)$$

and at least one monomer with the formula:

$$B{-}(Y)_m \qquad (2)$$

where monomers of formula (1) are polymerisable with monomers of formula (2), n and m are integers greater than or equal to 2, such that n and m may be the same or different, X is a group containing a terminal thiol, Y is a group containing a reactive unsaturated carbon-carbon bond, each X may be the same or different, each Y may be the same or different, and A and B are molecular fragments such that at least one of A or B is an organic charge-transporting or organic light-emitting fragment.

2. A composition according to claim 1, wherein $n + m > 4$

3. A composition according to any preceding claim wherein A, B, X, and Y do not contain any carbonyl groups.

4. A composition according to any preceding claim wherein at least one of A and B is a hole-transporting molecular fragment.

5. A composition according to any one of claims 1 to 3 wherein at least one of A and B is an electron-transporting molecular fragment.

6. A composition according to any one of claims 1 to 3 wherein at least one of A and B is a bipolar-transporting molecular fragment.

7. A composition according to any one of claims 1 to 3 wherein at least one of A and B is a luminescent molecular fragment.

8. A composition according to any preceding claim which also comprises an initiator and/or an emissive dopant and/or a charge transporting dopant

9. A solid film comprising a thermally-induced or radiation-induced polymerisation reaction product of a composition according to any one of claims 1 to 8.

10. A solid film comprising a radiation-induced polymerisation reaction product of a composition according to any one of claims 1 to 8 that has a pre-determined pattern.

11. A solid film comprising a polymer with repeat unit

-(A-Z-B-W)- (3)

where A and B are as defined above, Z is the addition product of the thiol-containing group, X, and the group containing a reactive unsaturated carbon-carbon bond, Y, and W is the addition product of the group containing a reactive unsaturated carbon-carbon bond, Y and the thiol-containing group, X.

12. An organic light emitting device comprising laminated in sequence a substrate, an electrode, a first optional charge transporting layer, an emissive layer, a second optional charge transporting layer and a counter electrode wherein at least one of the emissive layer, the first optional charge transporting layer or the second optional charge transporting layer is a film according to either claim 9, or claim 10, or claim 11.

13. An organic light emitting device comprising laminated in sequence a substrate, an electrode, a first optional charge transporting layer, an emissive layer, a second optional charge transporting layer and a counter electrode wherein the emissive layer is a film according to either claim 9 or claim 10 or claim 11.

14. A device as in claim 12 or 13 wherein the light emitting layer contains an emissive dopant.

15. A process for forming a device as claimed in claim 12, 13 or 14 that comprises the steps of:

i) depositing a film of a composition claimed in any one of claims 1 to 8; and

ii) exposing at least portions of said film to actinic radiation to polymerise the corresponding portions of the film.

16. A process according to claim 15 wherein the film is exposed to actinic radiation through a mask and the film is then developed to remove the unexposed portions of the film.

17. A process for forming a device as claimed in claim 13 or 14 that comprises the steps of:

i) depositing a film of a composition claimed in any one of claims 1 to 8 that is capable of emitting light of a first colour;

ii) exposing portions of said film to actinic radiation through a mask to polymerise the corresponding portions of the film;

iii) removing unexposed portions of said film to leave a pre-determined pattern;

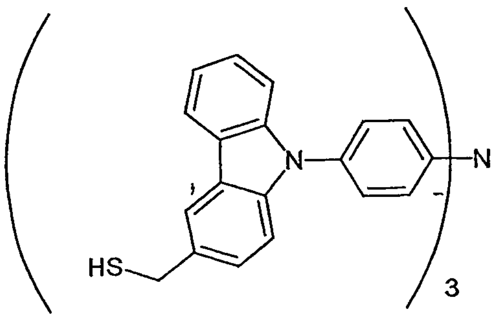
iv) depositing a film of a composition claimed in any one of claims 1 to 8 that is capable of emitting light of a second colour; and

v) exposing portions of said second colour film to actinic radiation through a mask to polymerise the corresponding portions of the film.

ABSTRACT

POLYMERISABLE COMPOSITIONS AND ORGANIC LIGHT-EMITTING DEVICES CONTAINING THEM

Compositions of a mixture of a thiol material and a material that contains a reactive unsaturated carbon-carbon bond that can be polymerised to form a charge-transporting or luminescent film are described, as is an organic light-emitting diode (OLED) device comprising at least one such charge-transporting or emissive layer that has been formed by polymerising a thiol material and an ene material. The process for forming such an OLED, including the deposition of a layer of material comprising the polymerisable composition, from solution, exposing said layer to actinic radiation through a mask, and then optionally developing said film to form a photopatterned film, is also disclosed.



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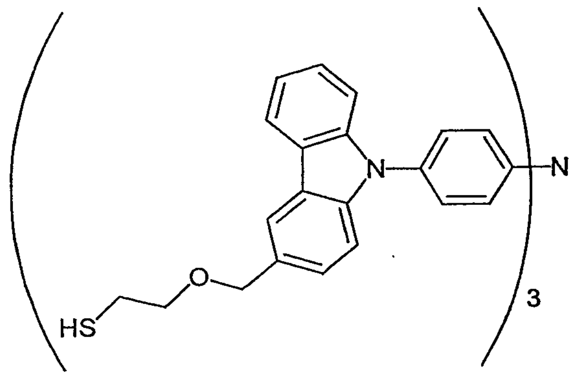

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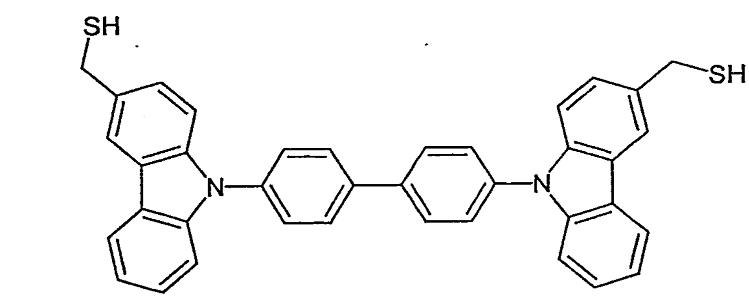
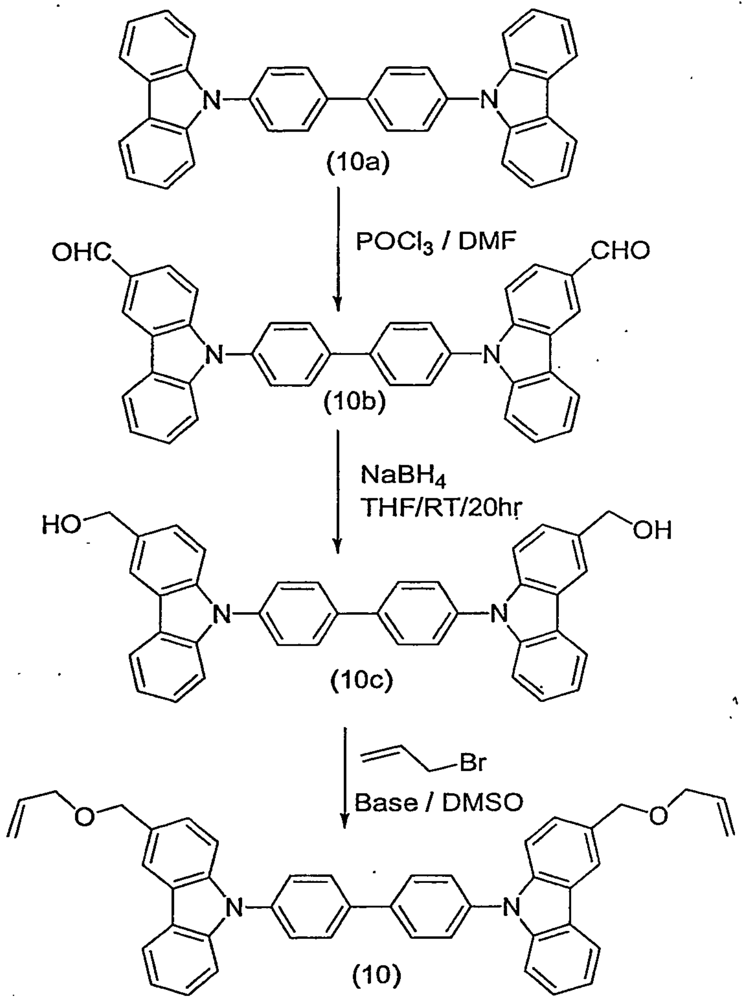
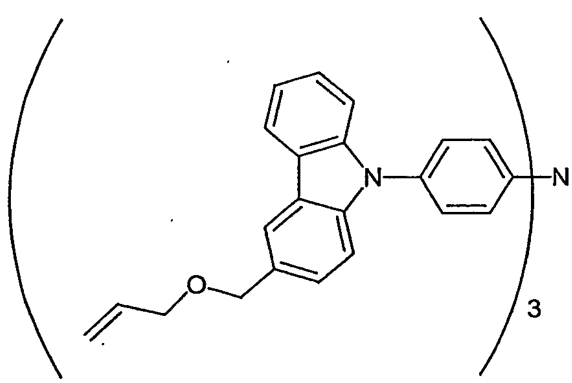


3

Figure 1


(10a)
POCl3 / DMF
OHC
CHO
(10b)
NaBH4
THF/RT/20hr
HO
OH
(10c)
Br
Base / DMSO
(10)


N
3

11

FIGURE 2